PB84-212240

TOX (Total Organic Halogen) Is It the Non-Specific Parameter of the Future

(U.S.) Municipal Environmental Research Lab.
Cincinnati, OH

Jun 84

U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-212240

EPA-600/D-84-169
June 1984

TOX, IS IT THE NON-SPECIFIC PARAMETER OF THE FUTURE?

by

Alan A. Stevens and Ronald C. Dressman
Drinking Water Research Division
Municipal Environmental Research Division
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

R. Kent Sorrell and Herbert J. Brass
Technical Support Division
Office of Drinking Water
U.S. Environmental Protection Agency
Washington, D.C. 20460

MUNICIPAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OH 45268

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/D-84-169	2.
3. RECIPIENT'S ACCESSION NO. PB84 212240	
4. TITLE AND SUBTITLE TOX, IS IT THE NON-SPECIFIC PARAMETER OF THE FUTURE?	5. REPORT DATE June 1984
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Alan A. Stevens and Ronald C. Dressman[a] Herbert J. Brass and R. Kent Sorrell[b]	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS [a]Drinking Water Research Division, MERL, ORD [b]Technical Support Division, ODW	10. PROGRAM ELEMENT NO. BNC1A
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Municipal Environmental Research Laboratory - Cin., OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268	13. TYPE OF REPORT AND PERIOD COVERED
	14. SPONSORING AGENCY CODE EPA/600/14
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

A total organic halogen (TOX) analysis directly measures halogen (Cl, Br, I) covalently bound to organic molecules in a sample. Currently, the most popular method for TOX in water involves carbon adsorption, oxidative combustion, followed by measurement of the formed hydrogen halide by microcoulometry. TOX can be used as an indicator of water quality and in water treatment for unit process design and control. TOX can be a direct measure of disinfection by-product formation or, in some circumstances, a surrogate measure of individual organic pollutants. Individual circumstances must be carefully judged to determine the usefulness of TOX in these applications.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 31
	20 SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

TOX, IS IT THE NON-SPECIFIC PARAMETER OF THE FUTURE?

by

Alan A. Stevens and Ronald C. Dressman
Drinking Water Research Division, MERL, ORD

R. Kent Sorrell and Herbert J. Brass
Technical Support Division
Office of Drinking Water
U.S. Environmental Protection Agency
Cincinnati, OH 45268

ABSTRACT

A total organic halogen (TOX) analysis directly measures halogen (Cl, Br, I) covalently bound to organic molecules in a sample. Currently, the most popular method for TOX in water involves carbon adsorption, oxidative combustion, followed by measurement of the formed hydrogen halide by microcoulometry. TOX can be used as an indicator of water quality and in water treatment for unit process design and control. TOX can be a direct measure of disinfection by-product formation or, in some circumstances, a surrogate measure of individual organic pollutants. Individual circumstances must be carefully judged to determine the usefulness of TOX in these applications.

INTRODUCTION

CARBON ADSORPTION APPROACH TO TOX

In the early 1970's in an effort to find ways to measure halogenated organic compound removal by granular activated carbon (GAC) filters at water treatment plants along the Rhine River, Kuhn and Sontheimer developed a technique (1,2) to measure the total organic chlorine (TOCl) adsorbed on the GAC at various depths of the filter, thus defining the adsorption wave front. The halogenated compounds found in the Rhine (3) were not naturally occurring and were, therefore, considered undesirable in a finished drinking water. The location of the adsorption wave front gave important information about the status of the carbon filters' ability to continue to remove these pollutants. If exhaustion were shown, it signaled the need for reactivation. The procedure developed by Kuhn involved the combustion of a one gram GAC sample in an atmosphere of O_2 and steam, followed by analysis of the liberated chloride with an ion-specific electrode. Further investigation by Kuhn et. al. (4) led to techniques for measurement of the TOCl content of the water itself.

The first step for water analysis involved the adsorption of the organic compounds from the water onto ground granular activated carbon. This was accomplished by adding one gram of the activated carbon to a 10-L water sample and stirring for one hour. This batch extraction was repeated a second time after recovering the activated carbon by a process of flocculation, sedimentation, siphoning off of the water, and membrane filtration.

The recovered carbon, in the form of a sludge from each extraction, was then pyrohydrolyzed to convert organochlorine compounds to HCl. In the pyrohydrolysis procedure, superheated steam and oxygen were passed through two furnaces in series having a common combustion tube, the first heated from ambient temperature to 700 C and the second maintained at 1000 C. The HCl produced during the pyrohydrolysis was collected as the pyrohydrolyzate by condensing the steam.

The measurement of the Cl^- in the pyrohydrolyzate was performed with a select-ion probe. To account for the interference from inorganic Cl^- adsorbed onto the activated carbon, a duplicate sample was extracted in the same way, and the recovered activated carbon sludge was washed in a solution of sodium nitrate for a minimum of six hours. In this process, NO_3^- displaced inorganic Cl^- from the carbon, and the Cl^- in the wash water was then measured with the select-ion probe. The calculation of Cl^- contributed by organochlorine compounds was then made by subtracting the amount of Cl^- measured in the nitrate washed sample from the amount of Cl^- measured in the pyrohydrolyzate. This value was termed TOCl.

As a result of an evaluation (5) by the Drinking Water Research Division (DWRD) of the Municipal Environmental Research Laboratory (MERL), USEPA, Cincinnati, Ohio, several modifications were made to the method of Kuhn and Sontheimer. Microcoulometry was selected to measure the Cl^- because of a positive bias associated with the use of the select-ion probe that was recognized to have produced values up to 10 times the true value in some surface water samples. The selection of the microcoulometric detector also increased sensitivity by 100-fold thus reducing the necessary sample size to 100 mL or less. The measurement was redefined as carbon adsorbable organohalides reported as Cl^- (CAOX as Cl^-). This definition recognizes that only the carbon adsorbable fraction of TOCl (90-95% as inferred from measured TOC adsorption) is being accounted for, and that Br^- and I^- when present were also being titrated. Next, inorganic X^- was excluded from the adsorption process by the addition of NO_3^- to the sample; the need for a duplicate sample to correct for inorganic Cl^- interference was thus eliminated, and with it the 6-hour delay in obtaining results. Finally, the X^- contributed by organohalides was determined directly on the activated carbon sludge from samples pretreated to exclude the adsorption of inorganic X^- onto the carbon, thus providing for increased reproducibility and much greater accuracy.

The evaluation of the Kuhn batch method led to the development of a mini-column method (6) for adsorbing organhohalides onto activated carbon, the evaluation of which by DWRD led to modifications by Dohrmann that represented the state-of-the-art for analysis of OX in water by oxidative combustion of the carbon. This measurement is generally referred to as Total Organic Halide (TOX) and is the basis of EPA Method 450.1, Total Organic Halogen, available from the Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

In addition to Dohrmann, Mitsubishi Chemical Industries Limited, through the OSA Instrument Corporation, is also marketing an instrument system consisting of a TOX analytical module and an adsorption module based on Method 450.1.

Instrumentation that employs the carbon adsorption concept followed by reductive pyrolysis and conductivity detection of the halide has has not proven to be reliable. In the authors' hands, problems included poor precision and accuracy, insufficient inorganic chloride rejection, and high variability of system blanks.

A small-batch (100 mL) extraction method using activated carbon has also been developed (7) that is a hybrid of the modified Kuhn method (5) and the mini-column method for water samples (6). The extraction is scaled down to treat a 100-mL sample. Activated carbon recovery is by membrane filtration without the need for flocculation and sedimentation. Pyrolysis and detection are the same as for the mini-column method. The results obtained by this method are essentially the same as those that would be obtained by the mini-column method.

OTHER APPROACHES TO OX

Another method for OX is the mini-column method that employs XAD resins as the adsorbent (8). It involves solvent desorption of OX from the resin, controlled combustion of a portion of the solvent sample and detection by microcoulometry. This method is not preferred because of unfavorable adsorption characteristics of some compounds with the resin.

Flash vacuum-evaporation is an OX method under study (9). It involves first a desalting step via steam generation and recondensation followed by the catalytic conversion of organohalides to Cl_2. The Cl_2 is then measured by a fluorometric derivatization analysis using syringaldazine.

Neutron activation (NA) followed by gamma ray spectroscopy has been used for the analysis of organohalogens. This technique was first reported used in Sweden (10). The method has been receiving increasing attention and is an excellent research tool. The organic halide can be isolated by either solvent extraction or carbon adsorption. Whether a solvent extraction is involved, which can account only for the lipophilic fraction of OX, or adsorption onto activated carbon is involved, NA can differentiate between the halogens that comprise TOX. It does not, however, fulfill the need for a routine analytical tool for use in water laboratories throughout the country.

"Extractable organic chlorine" (EOCl) was suggested as a useful indicator for chemical pollution in surface water (11). It was determined by extracting with petroleum ether and measuring the "total" organohalides in the extract by microcoulometry.

The ion chromatograph offers another possibility for the detection and measurement of individual halides such as would be recovered in a pyrohydrolyzate and reported as OX (5). Interferences that must be overcome occur as a result of the sulfur associated with carbon that is pyrolyzed.

Organic compounds in aqueous solutions can be separated on the basis of molecular weight using ultrafiltration membranes. These separations are not absolute, because some organic matter can be retained due to electrical charges on the organics. McCahill, Conroy and Maier (12) have used this concept to separate OX according to molecular weight. Following separation, the solutions are irradiated with UV radiation to cleave the C-X bond. The Cl^- is determined by select-ion electrode, whereas ion chromatography is used to determine the Cl^- and Br^- simultaneously. The photolysis required 1.5 hours, followed by a typical ion chromatographic analysis time of 0.3 to 0.5 hours. No detection limits were given, however, the ion chromatograph can detect 10-7 to 10-6M halogen with a 1 mL injection.

PURGEABLE ORGANIC HALIDE (POX) AND NON-PURGEABLE ORGANIC HALIDE (NPOX)

Analysis for POX is conducted directly by purging a 10-mL aliquot of the water sample directly into the pyrolysis furnace and titrating the HX in the effluent gas during the purge. Commercially available instruments have a built in capability for doing this. Instrument instruction manuals detail the use of this feature. POX can also be estimated by converting THM or other volatile organics data to units of Cl^- ion measurement (13).

Experience in the DWRD laboratory has shown that for most accurate results separate THM analysis for purgeable compounds and NPOX should be performed on disinfected water having an OX concentration of 150 ug/L or higher. This is desirable to avoid loss of some THMs that would occur during a TOX analysis. When it is necessary to determine POX and NPOX individually and directly, separate aliquots of the sample should be taken for each analysis. The aliquot taken for NPOX analysis can first be purged free of trihalomethanes. The NPOX aliquot can then be analyzed by the carbon adsorption method for TOX. The results for POX and NPOX analysis can then be combined to give a measure of TOX in the sample.

Generally, whenever either POX or NPOX is determined analytically, the other can be determined by subtraction from TOX. The failure of TOX measurement to account completely for THMs, however, means that NPOX determined by subtracting converted gas chromatographic results is biased low 10 to 20 percent (14).

MEASUREMENT OF DISINFECTION BYPRODUCTS

Disinfectants react with organic materials in drinking water sources and thus form byproducts of largely unknown composition. That these reactions occur has been long recognized in the form of disin-

fectant "demand" and natural organic color bleaching by chlorine, chlorine dioxide and ozone. Most of the demand is oxidative; that is, susceptible sites on the organic molecules are oxidized to new functionalities. In the process, the disinfectant is chemically reduced. On the order of 90% of chlorine demand, for example, can ultimately be accounted for as chloride ion. The remaining 10% or so may react by substitution or addition reactions and become incorporated into the organic molecular structure. Where bromide ion is present, oxidation to active bromine species also occurs, and bromine will also be found in the organic byproduct mixture (15).

Some specific compounds that result from this type of reaction have been identified. These include the trihalomethanes that are now regulated. Some others are dihaloacetonitriles, trichloroacetic acid, dichloroacetic acid, and 1,1,1-trichloroacetone. The above compounds can be identified and measured by gas chromatographic techniques. These and related compounds that are detectable by GC techniques do not, however, account for all of the organic halogen byproducts. Some of these other materials are high molecular weight non-volatile species that are not amendable to GC or other available analytical techniques capable of detecting and measuring specific compounds. Thus, the TOX, especially the NPOX parameter, becomes a useful non-specific measure of the degree of organic attachment of halogen (Cl, Br, I) in organic molecules as a result of the disinfection process and, therefore, a useful tool in unit process design and control.

Based on recent findings (16,17) that organic halogen formation is best avoided in drinking water treatment, the non-specific measurement technique can be used as a group parameter to measure treatment improvement or deterioration. This is illustrated by example in Figures (1) and (2). The data used to develop these figures were generated during studies in the DWRD Laboratory (18).

Figure 1 displays the results of free chlorination of 5 mg/L Aldrich humic acid solution at three temperatures, three different pH values over three different reaction periods and two chlorine concentrations. POX, determined by a THM measurement (essentially all chloroform) is displayed below the abscissa, and NPOX above. TOX is represented by the total bar. Bromide was not involved in this experimental matrix. The units are in ug/L as Cl^-.

In general, THMs are shown in Figure 1 to have increased with reaction pH, while NPOX decreased dramatically. At low pH, a temperature increase caused an increase in NPOX that did not occur at neutral and high pH values. Chloroform yield increased at all pH values with increasing temperature. NPOX concentrations approached their final values faster at high pH than at low pH. This effect was not observed for chloroform. Chlorine dose had a larger effect on NPOX concentrations than on chloroform. All of these results of chlorination are typical of those reported for humic materials obtained from other sources (19).

Figure 2 compares the NPOX and trihalomethane formation at 20C at 3 different pH levels for each of the three disinfectants: chlorine, chloramines, and chloride dioxide. NPOX formation was reduced by 85% when comparing the use of chloramine to chlorine as the disinfectant, and is still much lower when chlorine dioxide was used. Trihalomethane formation was reduced by greater than 95% when chloramines were used, and no trihalomethanes were detected when chlorine dioxide was used. Unlike with chlorine, which increases the formation of trihalomethanes with increasing pH, the use of chloramines and chlorine dioxide as disinfectants resulted in a decrease in the formation of all organic halides with increasing pH. NPOX formation with chlorine dioxide was rapid, with no difference observed between 2 hr and 144 hr sample concentrations.

These figures illustrate the variation in organohalide species formed under different conditions, giving clues of how to minimize OX formation during treatment. One must keep in mind, however, that this group parameter is measuring only one specific attribute of the sample's organic matrix; i.e., halogen content. The beginning assumption was that this was the most important byproduct characteristic of concern. TOX is not a total measure of disinfectant byproduct and may not even be proportional to it. This is clear from the data presented in figure 2 when one considers that the oxidant demands were similiar for chlorine and chlorine dioxide. Oxidant demand may indeed be a better non-specific parameter for disinfection byproducts if non-halogenated byproduct species are important. Thus, the usefulness of the TOX parameter as a measure of disinfection byproduct is limited by a lack of full knowledge of its significance.

USES AS A SURROGATE FOR SPECIFIC CHEMICALS

TOX has been incorporated into federal regulations for monitoring ground waters near hazardous waste sites (20). Its use as a surrogate has also been suggested for monitoring individual halogen containing VOCs in waters intended for drinking (21). This section will focus on TOX and POX as a measure of the presence of halo-VOCs in such waters.

For proper interpretation of TOX or POX results, it is necessary to understand the ability of these analytical techniques to reflect the concentration of specific halogen containing chemicals; i.e. the appropriate mass balances. Few investigations have been published correlating TOX and POX analyses with individual VOCs. Early data of TOX accuracy for volatile organohalides ranged from 73% to 110%, Table 1 (22,23). They included such compounds as chloroform, bromoform and bromobenzene in reagent water at concentrations of 98 to 443 ug/L. The POX data in Table II from the same authors (14,24) indicated 98% recovery for bromoform and 80% recovery for THMs. It should be pointed out that the 80% recovery for THMs was obtained with a vitrified insert tube in the measurement system, which was demonstrated to have caused a reduced recovery. A more nearly complete recovery of chloroform was obtained when the tube was replaced.

Additional POX recovery data were obtained for a wider variety of volatiles at higher concentrations by Riggin et al, Table III (25). These recoveries were also from reagent waters and dosed at 1000 ug/L.

They reported compound recoveries to be from 47 to 106%, which were from 11% lower (chloroform) to 51% lower (bromodichloromethane) than those previously reported (22,23).

At lower concentrations of the spiked VOCs, variable recoveries were observed by Riggin et al, Table IV (25). For 12.5 ug of chloroform per liter, a complete recovery was found. The other four compounds all afforded lower recoveries, with bromoform not being detected at a 30-ug/L concentration.

More recent data for VOC recoveries, Table V, were obtained using VOC-free ground water (26). This ground water was spiked, head-space free, with the volatile organics of interest. Each compound was studied at three concentrations, 10, 30 and 100 ug/L. The samples were analyzed in triplicate by both TOX and POX. Purge-and-trap/gas chromatography/electrolytic conductivity detector (P&T/GC/ElCD) analyses were also performed to ensure the concentrations in the sample bottles were close to their calculated values. Analysis by P&T/GC/ElCD also ensured the integrity of the spiked samples by revealing the presence, if any, of other VOCs.

The compounds at 10 ug/L, which is near to quantitation limit of the procedures, gave a recovery range of 79-140% for TOX and 25-88% for POX. The recoveries of the chlorinated compounds for the 30 and 100-ug/L concentration in Table V ranged from 55-80% recovery. There does not appear to be a clear relationship between concentration and recovery. However, there may be a more efficient recovery by TOX than for POX at the concentrations tested.

Results for an interlaboratory study (Table VI) provided similar findings, with TOX recoveries ranging from 73-91% and POX recoveries from 56-77% for the three volatile compounds (27). These data also seem to demonstrate slight recovery bias in favor of TOX. The results obtained by the two laboratories generally agreed within 10% of each other.

TABLE I

REPORTED ACCURACY OF TOX FOR VOCs IN REAGENT WATER

Model Compounds	Conc. ug/L	Average Recovery per cent	Reference
Chloroform	98	89	(22)
	112	94	(23)
Bromodichloromethane	160	98	(22)
Dibromochloromethane	155	86	(22)
	374	73	(22)
Bromoform	160	110	(22)
	238	100	(23)
Bromobenzene	443	95	(23)

TABLE II

REPORTED ACCURACY OF POX FOR VOCs IN REAGENT WATER

Model Compounds	Conc. ug/L	Average Recovery per cent	Reference
Bromoform	100	98	(24)
THMs	140	80[a]	(14)
Chloroform	-	100	(14)

[a]Vitrified combustion tube insert

TABLE III

RECOVERY FOR VARIOUS PURGEABLE ORGANIC HALIDE (POX) COMPOUNDS SPIKED AT 1000 ug/L INTO REAGENT WATER - DOHRMANN DX-20 SYSTEM (25)

Compound	Recovery per cent
Methylene chloride	87 (4)[a]
Chloroform	81 (3)
Trans 1,2-Dichloroethylene	106 (0.2)
1,1-Dichloroethane	84 (3)
1,1-Dichloroethylene	78 (2)
1,1,2,2-Tetrachloroethane	88 (6)
Tetrachloroethylene	86 (0.6)
Carbon Tetrachloride	86 (1)
1,1,2-Trichloroethane	76 (8)
1,2-Dichloropropane	76 (2)
Trichlorofluoromethane	79 (7)
Trichloroethylene	76 (2)
1,1,1-Trichloroethane	68 (10)
1,2-Dichloroethane	70 (4)
1,3-Dichloropropene	60 (4)
Chlorobenzene	48 (7)
1,2-Dichlorobenzene	65 (5)
1,3-Dichlorobenzene	51 (7)
1,4-Dichlorobenzene	61 (7)
Bromodichloromethane	47 (9)
Bromoform	64 (8)

[a]Relative standard deviation (%) in parentheses

TABLE IV

AVERAGE RECOVERY FROM 7 POX ANALYSES OF SELECTED COMPOUNDS (25)

Compound	Spike Level ug/L	Spike Level ug/L as Cl^-	Amount of POX Found ug/L as Cl^-	Recovery per cent
Chloroform	12.5	11	11 (1.4)[b]	100
Trichloroethene	14	10	6 (0.7)	60
Tetrachloroethene	14	10	5 (1.0)	50
Chlorobenzene	25	8	3 (0.6)	38
Bromoform[a]	30	13	ND	<10

ND = Not Detected.
[a]Recovery for bromoform at 300 ug/L (130 ug/L as Cl^-) was 48% and 49% for duplicate analyses.
[b]Standard deviation in parenthesis.

TABLE V

AVERAGE ACCURACY OF TOX, POX AND PURGE-AND-TRAP FOR DOSED VOC GROUND WATER SAMPLES[a] (26)

Compound	Calc. Conc. ug/L	TOX Recovery per cent	POX Recovery per cent	P&T Confirmation Analysis, per cent of dosed quantity
Bromoform	10.0	140[b]	62[b]	120
	30.5	93	66	100
	100	120[b]	91	110
Chloroform	10.0	79[b]	25[b]	94
	29.9	76	43[b]	110
	100	81	76	96
t-Dichloroethylene	10.1	84[b]	53	97
	30.1	63	55	90
	98.4	60	59	99
Tetrachloroethylene	9.83	79[b]	88[b]	91
	30.2	75	70[b]	100
	101	78	70	110

[a]Based on triplicate analyses for TOX, POX, duplicate for P&T.
[b]Precision was >10%; the ranges of these percent relative standard deviations were: 15%-61% at 10 ug/L; 22%-25% at 30 ug/L; 27% at 100 ug/L.

TABLE VI

INTERLABORATORY VOC RECOVERY STUDY (27)

Compound Spike ug/L	Recovery[a] per cent			
	TOX		POX	
	TSD[c]	DWRD[c]	TSD	DWRD
$CHCl_3$ (50)	81 (3.7)	90 (4.9)	77 (5.1)	56 (6.2)
$CHCl_3$ (150)	77 (1.0)	73 (9.7)	70 (1.6)	66 (4.2)
$CHBr_3$ (150)	85 (1.3)	87 (14.)	60 (1.5)	58 (11.)
t-DCE[b] (150)	76 (0.1)	91 (17.)	73 (3.1)	61 (8.2)

[a]Relative standard deviation for triplicate measurements are given in parentheses.
[b]t-DCE is trans-Dichloroethylene.
[c]TSD and DWRD are Technical Support Division and Drinking Water Research Division Laboratories respectively.

The VOC data presented thus far has predominately been from spiked reagent water or a single source of ground water. The ability of TOX and POX methods to measure the presence of VOCs in a variety of ground waters, and the methods' ruggedness, have not been fully investigated. Some information that has been gathered is shown in Table VII (26). All the cities listed in the table, utilize ground water sources. The TOX concentrations of these raw waters ranged from <5 ug/L as Cl^- to 300 ug/L as Cl^-. The POX results ran from <2 ug/L as Cl^- to 300 ug/L as Cl^-. PT/GC/ElCD was used to compare the TOX and POX concentrations with concentrations reported as chloride for individual VOCs. This comparison indicated that POX gave a positive result only when VOCs were present. TOX analysis on the other hand afforded positive results in all but one of the 11 samples. Five of these positive TOX samples contained no detectable VOCs.

Information collected by a USEPA survey, Table VIII (28), also indicated that a non-VOC background could interfere with the use of TOX as a surrogate for low concentrations of VOCs. The survey found an average TOX of 19 ug/L as Cl^- in raw ground water, ranging from <5 ug/L as Cl^- to 85 ug/L as Cl^-. A high TOX, 85 ug/L as Cl^-, did not indicate a high VOC concentration, as less than 1% could be accounted for by halogenated VOC in this sample. Surface waters, also seem to possess a variable TOX background, ranging from <5 to 49 ug/L as Cl^-. In both ground and surface water, the TOX analysis would have to detect VOC concentrations above the background interference, whose nature and variability are yet undefined.

SAMPLE STABILITY

Recent information has shown that, after chlorination, certain of the constituents comprising TOX are not stable when a water sample is stored. This aspect of TOX loss during sample storage was first revealed in a paper presented at an American Chemical Society meeting in 1981 (29). The paper dealt with storage of chlorinated drinking waters The first study, using samples from a surface water source stored at 20°C, revealed a 30% decrease in TOX concentration 15 days after addition of sulfite to reduce the chlorine residual (Figure 3). A 50% increase of TOX was observed when the chlorine residual was not reduced because of the dominance of continued TOX formation. The storage at subambient temperatures (5° C) of sulfite-reduced drinking water from the same source, demonstrated a slower rate of decline and a smaller percentage of loss of only 10%. Analysis of THMs, the main component of the purgeable fraction revealed no significant change in concentration, therefore, the decline was from the loss of nonpurgeable organohalides (NPOX). These losses are suggested to be due to decomposition of metastable organohalides formed during the chlorination process (30). Similar behavior has been observed in chlorinated ground water and tertiary effluents, with a 20% loss of TOX after reduction of the chlorine residual (31).

The storage of sulfite-reduced samples at subambient temperatures is not, however, a guarantee of low NPOX losses. Data for other surface supplied drinking waters stored under identical conditions show significant loss with time (Table IX) (30).

A suitable approach to solve this problem may be to acidify the sample and store it at reduced temperatures. In an experiment where one set of samples was acidified with nitric acid to pH 2, the TOX declined by only 15% after three months at room temperature (Table X) (30). A second set, whose pH was allowed to remain at 7.9, had a 51% loss during the same period. When acidification was used in combination with refrigeration, better preservation was afforded (Table XI). The acidified samples had no loss of TOX by day four and only a 6% loss by day 48. The unacidified samples (pH 7.9) suffered a 17% decline by day four and a 32% loss by day 48.

A parallel technique utilizes sulfuric acid and sodium sulfite along with refrigeration for stabilization of TOX (32). It has the reported advantage of allowing prepared sample bottles, containing both the sulfite and sulfuric acid, to be sent to the sampling site by air freight. Nitric acid cannot be readily shipped by air express. The effectiveness of sulfuric acid appears to be comparable to nitric. When used in conjunction with refrigeration, only a 9 percent loss of the TOX in the sulfite-reduced finished water (surface water source) was observed after 39 days of storage.

Losses observed for samples previously stored at either or both pH 5 and 6 C and then stored at either or both pH 9 and 20 C support the discussion on sample stability. This information was acquired during the disinfection byproduct studies previously discussed in relationship to figures 1 and 2.

TABLE VII

COMPARISON OF TOX, POX AND PURGE-AND-TRAP VOC CONCENTRATIONS

(ug/L as Cl^-) FOR SELECTED GROUND WATERS[a] (26)

City #	TOX	POX	VOCs via P&T
66951	21 (21)	<2	ND
66989	10 (56)	<2	0.3 (4)
66952	18 (46)	<2	0.6[b]
66990	27 (10)	21 (5)	20 (7)
66954	30 (15)	<2	ND
66991	20 (12)	<2	ND
66993	25 (27)	<2	ND
66998	9 (50)	<2	ND
66999	10 (5)	2 (50)	6 (6)
67000	<5	<2	ND
Riv[b]	300 (2)	300 (2)	330[b]

[a]Based on Triplicate Analyses for TOX and POX; Duplicate for P&T; the percent relative standard deviation (or per cent difference for P&T) are given in parenthesis.
[b]Denotes single analysis only
ND = Not Detected

TABLE VIII

TOX CONCENTRATION OF GROUND AND SURFACE WATER IN THE

CWSS RESAMPLE SURVEY (28)

No. of Sites	Water Type	TOX ug/L as Cl^-	VOC per cent[a]
12	Ground	<5-85 (avg = 19)	<1-39
6	Surface	<5-49 (avg = 20)	<1

[a]Defined as the percentage of TOX accounted for by VOCs.

TABLE IX

TOX DECLINE FROM SULFITE REDUCED DRINKING WATERS

(SURFACE WATER SOURCES) WITH SAMPLES STORED AT 5°C. (30)

Sample #	Date Sampled	Initial Conc.[a] ug/L as Cl^-	Storage days	Loss per cent
001-06	May 81	110 (3%)	191	39
006-03	Jan 81	430 (6%)	213	43
006-04	Feb 81	410 (2%)	183	41
006-05	Mar 81	520 (2%)	196	42
006-06	Apr 81	370 (1%)	165	39
008-01	Dec 80	120 (1%)	254	44
008-07	Jul 81	140 (15%)	30	28
017-02	May 81	120 (2%)	176	38
IWS	Jul 80	250 (2%)	21	18

[a]Based on duplicate analysis with precision given as

$$\% \text{ Diff} = \frac{A-B}{\frac{A+B}{2}} \times 100$$

TABLE X

COMPARISON OF TOX DECLINE FOR NITRIC-ACIDIFIED AND NON-ACIDIFIED TAP WATERS (SURFACE WATER SOURCE) STORED AT AMBIENT TEMPERATURES (30)

	pH 7.9		pH 2.0	
Day	Conc.[a] ug/L as Cl^-	Loss per cent	Conc.[a] ug/L as Cl^-	Loss per cent
0	160 (4.8%)	-	160 (4.8%)	-
10	120 (2.8%)	25	140 (5.5%)	8
89	76[b]	51	130[b]	15

[a]Based on duplicate analysis with precision given as

$$\% \text{ Diff} = \frac{A-B}{\frac{A+B}{2}} \times 100$$

[b]Single analysis

TABLE XI

COMPARISON OF TOX DECLINE FOR NITRIC-ACIDIFIED AND NON-ACIDIFIED TAP WATER (SURFACE WATER SOURCE) STORED AT 5°C. (30)

	pH 7.9		pH 2.0	
Day	Conc.[a] ug/L as Cl^-	Loss per cent	Conc.[a] ug/L as Cl^-	Loss per cent
0	140 (2.0%)	-	140 (2.0%)	-
4	110 (2.3%)	17	140 (9.7%)	-
48	94 (10%)	32	130 (3.2)	6

[a]Based on duplicate analysis with precision given as

$$\% \text{ Diff} = \frac{A-B}{\frac{A+B}{2}} \times 100$$

AVAILABILITY AND COST

Due to the Resource Conservation and Recovery Act (RCRA) requirements (33) and general interest in TOX as a surrogate, the use of TOX has become more widespread. At present, it is estimated there are between 50 and 75 commercial laboratories and universities that perform TOX analysis using the Dohrmann DX-20 system (34).

A survey was conducted by the Technical Support Division (TSD) in order to determine the capabilities of these laboratories. Thirty-three laboratories were contacted. This is about half of the laboratories that perform TOX analyses using the DX-20 system. Of these 33, only 18 performed POX analyses on a routine basis. Based on this survey, it is estimated that approximately half of all laboratories performing TOX analyses analyze for POX.

These same laboratories were asked to provide price quotes for the measurement of TOX, POX and trihalomethanes (THMs) by purge-and-trap and liquid-liquid extraction techniques. Also requested were quotes for the analyses by purge-and-trap of volatile organic chemicals containing halogen (VOCs). These VOC quotes were further identified as to the type of detector being used; namely, electrolytic conductivity (ElCD) or mass spectrometer. The cost information is shown in Table XII. TOX by Method 450.1 requires duplicate analysis for each sample, and this was also applied to POX. The prices for THM and VOC analyses are based on a single measurement because a duplicate is not required according to their respective methods. No information was obtained on the quality of analytical data generated by these laboratories.

The average cost for TOX and POX analyses were $99 and $77 respectively. The ranges of cost for sample analysis (Table XII) are great, varying by approximately an order of magnitude. Considering the fact that TOX measurements are much more routinely made when compared to POX, may account for the apparent elevation in the cost of POX analysis.

Based on the limited number of laboratories responding, THM measurements by purge-and-trap had an average price of $86 per sample and was more costly than measurement by liquid-liquid extraction, which had an average price of $59 per sample. The ranges of cost for THM sample analysis varied approximately five fold for purge-and-trap and two fold for liquid-liquid extraction. These cost data show that there is no cost saving in using TOX or POX as surrogate measures of the presence of THMs. In fact, based on average costs of analysis per sample, the determination of the four THMs is less expensive than the cost for total organohalide measurement.

Analysis of halogen containing VOCs had an average price of ($114) per sample with a range of $65 to $150. Based on information from a limited number of responding laboratories, analytical cost is more expensive than for either TOX and POX measurements.

General caveats must be placed on the above cost comparisons. The basis for contacting laboratories was in their ability to perform TOX

TABLE XII

COST COMPARISON OF ANALYSES

Analysis	Average Cost dollars	Cost Range dollars	Number of labs
TOX	99	30-200	33
POX	77	15-140	18
THM (P&T/GC/ELCD)[a]	86	42-200	15
THM (LLE/GC/ECD)[b]	59	40-85	8
VOC (P&T/GC/ELCD)[c]	114	65-150	5
VOC (P&T/GC/MS)[d]	207	100-350	18

[a]Trihalomethane analysis by EPA purge-and-trap methods using an electrolytic conductivity detector.
[b]Trihalomethane analysis by EPA liquid-liquid-extraction methods using an electron capture detector.
[c]Volatile organic analyses by EPA purge-and-trap methods using an electrolytic conductivity detector.
[d]Volatile organic analyses by EPA purge-and-trap methods using a mass spectrometer detector.

measurements using the Dohrmann, DX-20 system. THM and VOC cost data from these laboratories may not accurately reflect analytical costs for a wide range of laboratories. These costs appear reasonable, however, based on the direct experience of the authors in dealing with laboratories specializing in THM and VOC measurement.

Another point is that while these cost data were valid at the time the survey was performed (early 1984), little is known about changes in the cost of sample analyses in the future. Sudden increases or decreases in demand for a particular measurement could radically alter these cost data. Also, while not being actively considered at this time, lifting the requirement for duplicate analyses could considerably reduce the cost of sample analysis by the OX methods.

SELECTION OF ANALYTICAL APPROACH

Discussion in the previous sections focused on the following aspects of organohalide as a nonspecific parameter: the measurement procedures; use as a surrogate for disinfection byproducts; use as a surrogate for specific organic chemicals, principally VOCs; sample stability; and cost and relative ease of analysis. The emphasis in

this section is to relate what is known about organohalide and specific chemical analyses in an attempt to evaluate the utility of each measurement approach for activities such as surveying water quality; compliance monitoring; and unit process design, control and monitoring.

A word about matching methods to objectives is in order here. A key consideration is to establish the needs of the project, be it research, surveillance, or compliance monitoring. In some applications the selection of methodology capable of providing data of fine distinction and the highest possible precision and accuracy with stringent quality assurance requirements would be the primary consideration. In more routine applications, perhaps because of high sample volume, cost may be the primary consideration, and a method capable of providing data to a satisfactory but somewhat lesser degee of reliability and less stringent quality assurance requirements may be chosen. Should any uncertainty arise in the course of this latter approach, a more definitive method can be called into use as needed to resolve the question.

In either case, another primary consideration may be the amount of information that the method can provide; such as, specific compound identification and quantification vs the collective measurement of groups of compounds, a consideration that may be determined by the use of the data.

Figure 4 is a schematic diagram that links the relationship of water sample type to classes and subclasses of target organohalides. In addition, the diagram links the target to the selection of an appropriate method based on the type of response characteristic for that method.

Response characteristics are generally of three types. The first type is a combination of non-specific and non-exclusive, meaning that it does not measure specific compounds and can not be made to measure individual subclasses of compounds to the exclusion of other subclasses present to which the method responds. For example, POX will collectively measure THMs and halogenated volatiles such as TCE, whether one is interested in both subclasses or not.

The second type is a combination of specific and exclusive, meaning that it measures individual compounds to the exclusion of compounds present and belonging to other subclasses to which the method responds. For example, P&T/GC can be made to measure individual THMs to the exclusion of volatiles such as TCE, simply because of the gas chromatographic character of the method, even though both subclasses may be present in the sample. Each method of the second type is specific and exclusive only to a degree, however, that is determined by details of test procedures employed. The fine distinctions among these method types is beyond the scope of this paper.

The distinction about exclusivity is of special importance when using the OX methods as surrogates to estimate the presence of a defined subclass of organohalides. For example, in groundwater compli-

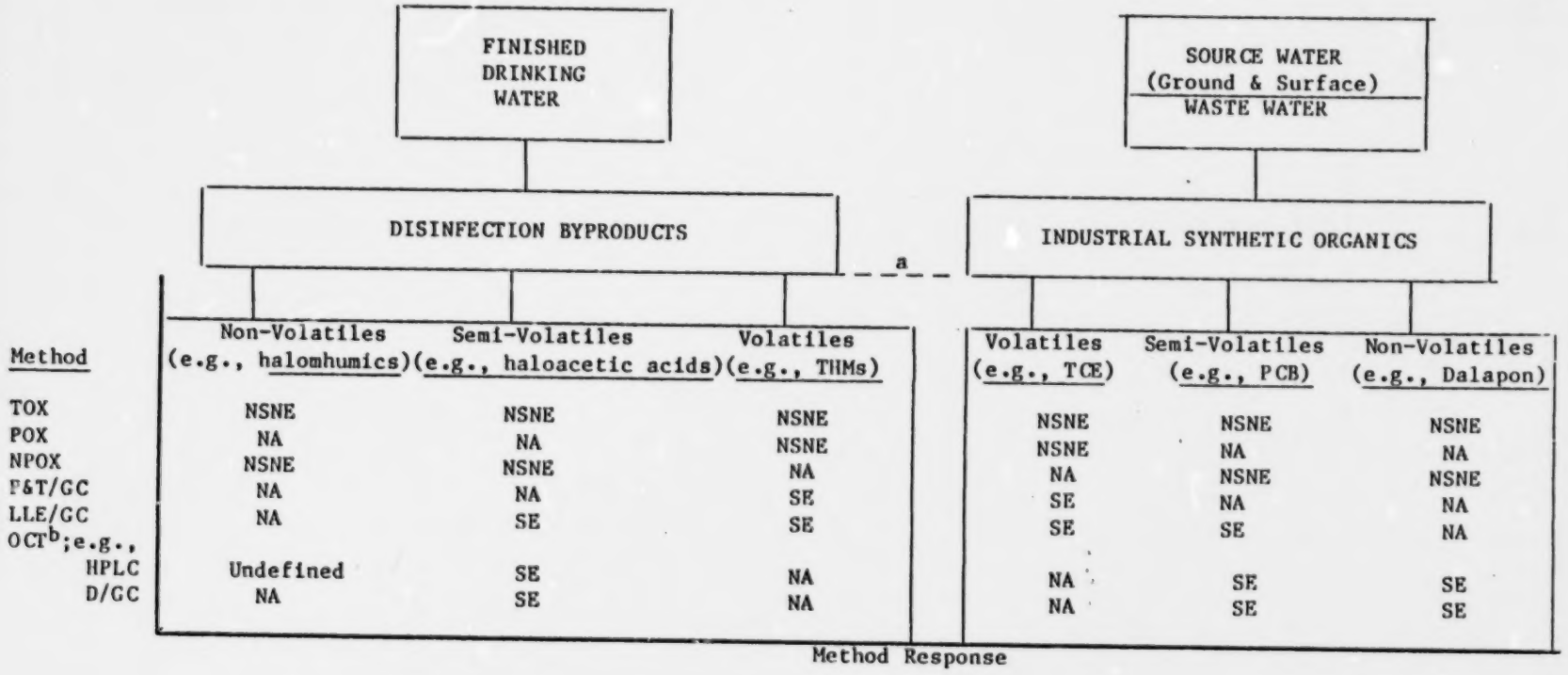
FINISHED DRINKING WATER
SOURCE WATER (Ground & Surface)
WASTE WATER
DISINFECTION BYPRODUCTS
a
INDUSTRIAL SYNTHETIC ORGANICS
Method
Non-Volatiles (e.g., halomhumics)
Semi-Volatiles (e.g., haloacetic acids)
Volatiles (e.g., THMs)
Volatiles (e.g., TCE)
Semi-Volatiles (e.g., PCB)
Non-Volatiles (e.g., Dalapon)
TOX NSNE NSNE NSNE NSNE NSNE NSNE
POX NA NA NSNE NSNE NA NA
NPOX NSNE NSNE NA NA NSNE NSNE
P&T/GC NA NA SE SE NA NA
LLE/GC NA SE SE SE SE NA
OCT[b];e.g.,
HPLC Undefined SE NA NA SE SE
D/GC NA SE NA NA SE SE
Method Response

FIGURE 4. SCHEMATIC LINKING THE RELATIONSHIPS OF WATER SAMPLE TYPE TO CLASS AND SUBCLASS OF TARGET ORGANOHALIDES TO METHOD RESPONSE.

NSNE = non-specific and non-exclusive - does not measure individual compounds and cannot be made to measure individual subclasses to the exclusion of others present to which the method responds.
NA = not applicable - does not measure the indicated subclass or individuals therein.
SE = specific and exclusive - measures individual compounds and can be made to measure compounds in individual subclass to the exclusion of compounds present belonging to other subclasses to which the method responds.

[a]The dotted line linking the classes of target organohalides suggests the possibility of both classes of compounds being present in some samples of all types.
[b]Other chromatographic techniques where D/GC = Derivitization/Gas Chromatography and HPLC is High Performance Liquid Chromatography.

ance monitoring, unless one has good reason to believe - perhaps by having previously characterized the water by specific compound analysis - that only the subclass of organohalides of interest are present, one must recognize that an OX measurement may be positively biased by the presence of organohalides other than those of the subclass of interest.

The third type of response characteristic is that a method is not applicable, meaning that it does not measure a particular subclass of compounds or any such individual compounds under the subclass.

The target organohalides defined in Figure 4 are differentiated based on chemical nature and origin. A class separation has been made between chemicals generated by disinfection, and chemicals that generally are regarded as industrial in origin. In each category there are volatile, semi-volatile and non-volatile halogen containing components. Of course, certain chemicals may be of volatility intermediate to these subclasses. While these cases are not directly dealt with here, they may be important in certain situations. Table XIII presents those methods considered by the authors to provide the most reliable measure of the various subclasses of organohalides for the activities discussed.

For disinfection byproducts, the volatile compounds are principally comprised of trihalomethanes. Other semi-volatile chemicals such as the dihaloacetonitriles and chloroacetones are known to readily occur at much lower concentrations than THMs. Although reporting on

conditions far more severe with regard to precursor and oxidant concentration than encountered in normal treatment practice, a substantial portion of this fraction has recently been identified as being comprised of lower molecular weight haloacetic acids (35). The non-volatile fraction includes halogenated precursor material, much of which is of high molecular weight.

For the analysis of disinfection byproduct volatiles, purge-and-trap (P&T) or liquid-liquid extraction (LLE) gas chromatography (GC) are preferred over a TOX, NPOX or POX measurement because GC analysis provides significantly more information; namely, the identities and concentrations of specific compounds. The analysis time and cost are approximately the same for organohalide and GC procedures because EPA, EMSL Method 450.1, unlike the other methods, requires duplicate analyses on every sample.

This requirement for duplicate analyses on every sample was originally stated in the context of some drinking water research activities where small differences and difficult to measure OX concentrations required greater stringency of quality control. The requirement could be lifted for some surveillance or monitoring activities when fine distinctions are not to be made between measurements. When fine distinctions need to be made, this requirement for replicate analysis may be applied to all analytical methods.

For many non-volatile byproducts, no alternative to organohalide measurement (NPOX) exists because either analysis for specific organics cannot be performed, or the compounds are either or both unknown and

TABLE XIII

MOST RELIABLE MATCH OF METHOD TO SUB-CLASS OF TARGET ORGANOHALIDES

	DISINFECTION BYPRODUCT			INDUSTRIAL SYNETHETIC ORGANICS		
Method	Non-Volatiles e.g., halohumics	Semi-Volatiles e.g., haloacetic acids	Volatiles e.g., THMs	Volatiles e.g., TCE	Semi-Volatiles e.g., PCB	Non-Volatiles i.e., dalapon
TOX	S - TOTALS MEASUREMENT - GENERAL INDICATOR OF OX CONTAMINATION					
POX			S	S		
NPOX	X					
P&T/GC			X	X		
LLE/GC		X	X	X	X	
HPLC					X	X
D/GC		X				X

S = currently useful as a screening procedure

D/GC = Derivitization/Gas Chromatography

difficult to measure. Certain semi-volatiles such as the chloroacetic acids, however, are amenable to LLE and derivitization/gas chromatography (D/GC) analysis, which is listed with other chromatographic techniques (OCT) in figure 4. OCTs such as column chromatography and high performance liquid chromatography (HPLC) are being used to identify higher molecular weight byproduct fractions. Generally, these OCTs are being used in research investigations.

The only way to directly measure non-volatile byproducts (NPOX) is to measure the NPOX by the method for TOX on a sample that has been purged completely free of volatiles. If a POX measurement is then made on a duplicate sample, the sum of the POX and NPOX thus obtained is equivalent to a TOX measurement (14). Alternatively, one can obtain an indirect measure of NPOX by directly measuring and subtracting the POX concentration from the TOX concentration (14).

One should keep in mind that both TOX and NPOX are measured to an unknown degree of accuracy because there exists no reference material of a humic/fulvic acid nature with which to assess recovery efficiency by carbon adsorption. The only estimate of accuracy comes from comparing TOC measurements before and after a sample has been put through the carbon. The efficiency of removal has been determined to be 90 to 95% (22) and is assumed to be the same for TOX.

In assessing contaminants which are industrial in origin, POX and TOX have been evaluated as surrogate measures of VOCs. In most cases, specific compound analyses are suggested, again due to enhanced information obtained relative to surrogate measurements at comparable cost and time. The potential does exist, however, for the use of POX as a surrogate for VOCs. The analytical cost survey reported in Table XII indicates average costs of $77 and $114 for POX and P&T/GC analyses, respectively. POX may become the preferred tool with which to screen for VOCs in certain situations if it is firmly established that duplicate analyses on every sample are not required. However, a negative but resolvable consideration must first be dealt with; namely, sufficient data must be acquired upon which to adequately demonstrate the relationship between POX and VOCs in a variety of surface and ground waters.

For semi-volatile and non-volatile industrial synthetic organohalides, TOX, NPOX, LLE/GC, and OCT analyses such as HPLC and D/GC are available. The relationship between these surrogate and nonsurrogate parameters has not been adequately shown. Some waters contain OX materials that are not accounted for by chromatographic techniques, whereas the accuracy of OX by carbon adsorption is uncertain.

Once again, specific chemicals should be measured if this can be accomplished at reasonable cost. However, the wide variety of organohalides which may exist at a given site, such as a landfills, can make TOX or NPOX measurement cost effective as a screening tool for halogen containing organics. If a "high" TOX or NPOX value were obtained during screening, specific compound measurements would then be attempted.

SUMMARY AND CONCLUDING REMARKS

We have seen that both surrogate measurements and specific compound determinations can be useful in assessing water quality. In some cases, specific chemical analyses provide the required information. However, in other situations, halogen containing chemicals either cannot be easily measured or cannot be measured at all, and TOX or NPOX can be useful as an indicator of chemical content.

For a survey of possible organohalide contamination, the organohalide measurements may be entirely satisfactory for the information they provide as a prelude to more detailed analysis, or simply as an early warning indicator.

An important application of organhalide measurement is in unit process design, control and monitoring. Waste water organohalide measurement discerns compounds primarily of industrial origin. Finished drinking water analysis primarily discerns disinfection byproducts.

In the earlier section dealing with the measurement of disinfection byproducts, a discussion of THM and NPOX data generated under sets of carefully controlled "treatment" conditions provides an excellent example of this unit process application. Information derived from these types of data can lead to treatment plant design which minimizes the formation, and thus the concentration of disinfection byproducts in the treated water. Byproducts can be monitored and to some extent controlled in the operation of the plant.

One assumes that, from a health standpoint, it is desirable to minimize these halogen containing constituents. One must realize, however, that in minimizing these constituents, an attempt is being made to control chemicals that, in most cases, cannot be directly measured. The difficulty in placing a value on this type of measurement is in the uncertainty of whether specific chemicals of health concern have in fact been controlled. In addition, non-halogen containing chemicals are not being considered. Controlling organohalide disinfection byproducts may have little or no relationship to the control of non-halogen containing compounds that are of health concern.

A dotted line connects disinfection byproducts to industrial synthetic organics in Figure 4. The dotted line is there to draw attention to the fact that many water samples have some potential for containing both classes of compounds. One should be aware that organohalide methods, being non-exclusive, have the hidden potential for biasing any attempted exclusive measure of either class of target organohalides.

In spite of the shortcomings discussed in this paper, the TOX method does have a unique advantage. It can demonstrate the absence of organohalide contamination without the need to resort to a variety of specific methods to eliminate all the possibilities. The cost savings of monitoring any situation with one method where two or more might otherwise be required, should be obvious. If one needs to demonstrate the absence either of volatile organohalides or non-volatile organohalides, POX and NPOX can be used to similar advantage.

REFERENCES

1. Kuhn, W., Sontheimer, H., Several Investigations on Activated Carbon for the Determination of Organic Chloro-Compounds. Vom Wasser, 15:65 (1973).

2. Kuhn, W., Sonthemier, H., Analytic Determination of Chlorinated Organic Compounds with Temperature-Programmed Pyrohydrolysis. Vom Wasser, 41:1 (1975).

3. Kolle, W., Sontheimer, H., Stieglitz, L., Qualification Test of Activated Carbon for Water Works Based on Its Adsorption Properties for Organic Chlorine Compounds. Vom Wasser, 44:203 (1975).

4. Kuhn, W., Fuchs, F., Sontheimer, H., Z. Wasser Abwasser Forsch., 10:6:162 (1977).

5. Dressman, R., McFarren, E., and Symons, J., An Evaluation of the Determination of Total Organic Chlorine (TOCl) in Water by Adsorption onto Ground Granular Activated Carbon, Pyrohydrolysis and Chloride-Ion Measurement. Proc. 5th AWWA WQTC, Kansas City, MO; (1977).

6. Takahashi, Y., Analysis Techniques for Organic Carbon and Organic Halogen. Proc. EPA/NATO-CCMS-Conference on Adsorption Techniques, Reston, VA (1979).

7. Jekel, M., Roberts, P., Total Organic Halogen Measurements for the Characterization of Reclaimed Waters: Occurrence Formation and Removal. Environ. Sci. & Technol., 14:970 (1980).

8. Glaze, W., Peyton, G., Rawley, R., Total Organic Halogen as Water Quality Parameters: Adsorption/Microcoulometric Method. Envir. Sci. & Technol., 11:685 (1977).

9. Gulf South Research Institute, Total Organic Chlorine (TOCl) Analysis Instrumentation for Direct Determination in Water Without Preconcentration. USEPA, EMSL, Cincinnati, OH; Grant No. 805340.

10. Lunde, G., Gether J., Josefsson, B., The Sum of Chlorinated and of Brominated, Non-Polar Hydrocarbons in Water. Bull. of Envir. Contam. and Tox. 13:656 (1975).

11. Wegman, R., Greve, P., The Microcoulometric Determination of Extractable Organic Halogen in Surface Water; Application to Surface Water; Application to Surface Waters of the Netherlands. The Sci. of the Total Envir., 7:235-245 (1977).

12. McCahill, M., Conroy, L., Maier. ., Determination of Organically Combined Chlorine in High Molecu ar Weight Aquatic Organics. Envir. Sci. & Technol., 14: 201 (1980).

13. Dressman, R., Procedure for the Application of the CAOX-as-Cl Method to Disinfected Water. Addendum ibid 5.

14. Dressman, R. and Stevens, A., The Analysis of Organohalides in Water-an Evaluation Update. Jour. AWWA, 75:8:431 (Aug. 1983).

15. Bunn, W., Haas, B. Deane E., Kleopfer, R., Formation of Trihalomethanes by Chlorination of Surface Water. Envir. Letters, 10:205 (1975).

16. Meier, J., Lingg, R., Bull, R., Formation of Mutagens Following Chlorination of Humic Acid - A Model for Mutagen Formation During Drinking Water Treatment. Mutation Research, 118:25 (1983).

17. Coleman, E., et. al., GC/MS Analysis of Mutagenic Extracts of Aqueous Chlorinated Humic Acids - A Comparison of the Byproducts to Drinking Water Contaminants. Submitted to Envir. Sci. & Technol.

18. Stevens, A., Moore, L., Dressman, R., Seeger, D., Disinfectant Chemistry in Drinking Water - Overview of Impacts on Drinking Water Quality. Presented Before the Division of Environmental Chemistry, ACS, Washington, DC; (Sept. 1983).

19. Fleischacker, S., Randke, J., Formation of Organic Chlorine in Public Water Supplies. Jour. AWWA 75:132 (March 1983).

20. USEPA, Standards and Interim Status Standards for Owners and Operators of Hazardous Waste Treatment, Storage, and Disposal Facilities. Fed. Reg., 45:98:33240 (May 19, 1980).

21. USEPA, National Revised Primary Drinking Water Regulations, Volatile Synthetic Organic Chemicals in Drinking Water; Advanced Notice of Proposed Rulemaking. Fed. Reg., 47:43:9352 (Mar. 4, 1982).

22. Dressman, R., Najar, B., and Redzikowski, R., The Analysis of Organohalides (OX) in Water as a Group Parameter. Proc. 7th AWWA WQTC, Philadelphia, PA; (1979).

23. Takahashi, Y. and Moore, R., Measurement of Total Organic Halides (TOX) in Water by Carbon Adsorption/Microcoulometric Determination. Presented at the 177th National Meeting of the American Chemical Society, Div. of Envir. Chem., Honolulu, HI; (1979).

24. Takahashi, Y., Moore, R., and Joyce, R., Measurement of Total Organic Halides (POX) in Water Using Carbon Adsorption and Microcoulometric Determination. Presented at the 179th American Chemical Society, Div. of Envir. Chem., Houston, TX; (1980).

25. Riggin, R., et.al., Development and Evaluation of Methods for Total Organic Halide and Purgeable Organic Halide in Wastewater. USEPA, EMSL, Cincinnati, OH; EPA-600/54-84-008 (Jan. 1984).

26. Sorrell, R. K., Daly, E., Boyer, L., and Brass, H. J., Monitoring for Volatile Organohalides Using Purgeable and Total Organic Halide Analyses as Surrogates. Presented at 5th Conference on Water Chlorination, Environmental Impact and Health Effects, Williamsburg, VA June 3-8, 1984.

27. Sorrell, R., Contner, G., and Dressman, R., USEPA, TSD/MERL; Unpublished Data.

28. Preliminary Report - Community Water Supply Survey-Resample. USEPA, Drinking Water Quality Assessment Branch, TSD, Cincinnati, OH; (1981).

29. Sorrell, R., Total Organic Halide: Occurrence, Stability and Process Control in Drinking Waters. Presented at the 181st National Meeting of the American Chemical Society, Div. of Envir. Chem., Atlanta, GA; (March 1981).

30. Sorrell, R., Stability of Total Organic Halide in Environmental Water Samples. Submitted to Envir. Sci. & Technol.

31. Hopkins, G., Environ. Eng. and Sci., Stanford U., Stanford, CA; Personal Communication.

32. Banovic, J., Water Research Laboratory, City of Columbus, Columbus, OH; Personal Communication.

33. USEPA, Hazardous Waste Management System, Part VII; Standards and Interim Status Standards for Owners and Operators of Hazardous Waste Treatment, Storage, and Disposal Facilities. Fed. Reg., 45:98:33239 (1980).

34. Dohrmann Division, Xertex Corporation, Santa Clara, CA; Personal Communication.

35. Christman, R., Norwood, D., Millington, D., Johnson, D., Stevens, A., Identity and Yields of Major Halogenated Products of Aquatic Fulvic Acid Chlorination. Envir. Sc. & Technol., 17:10:625 (1983).

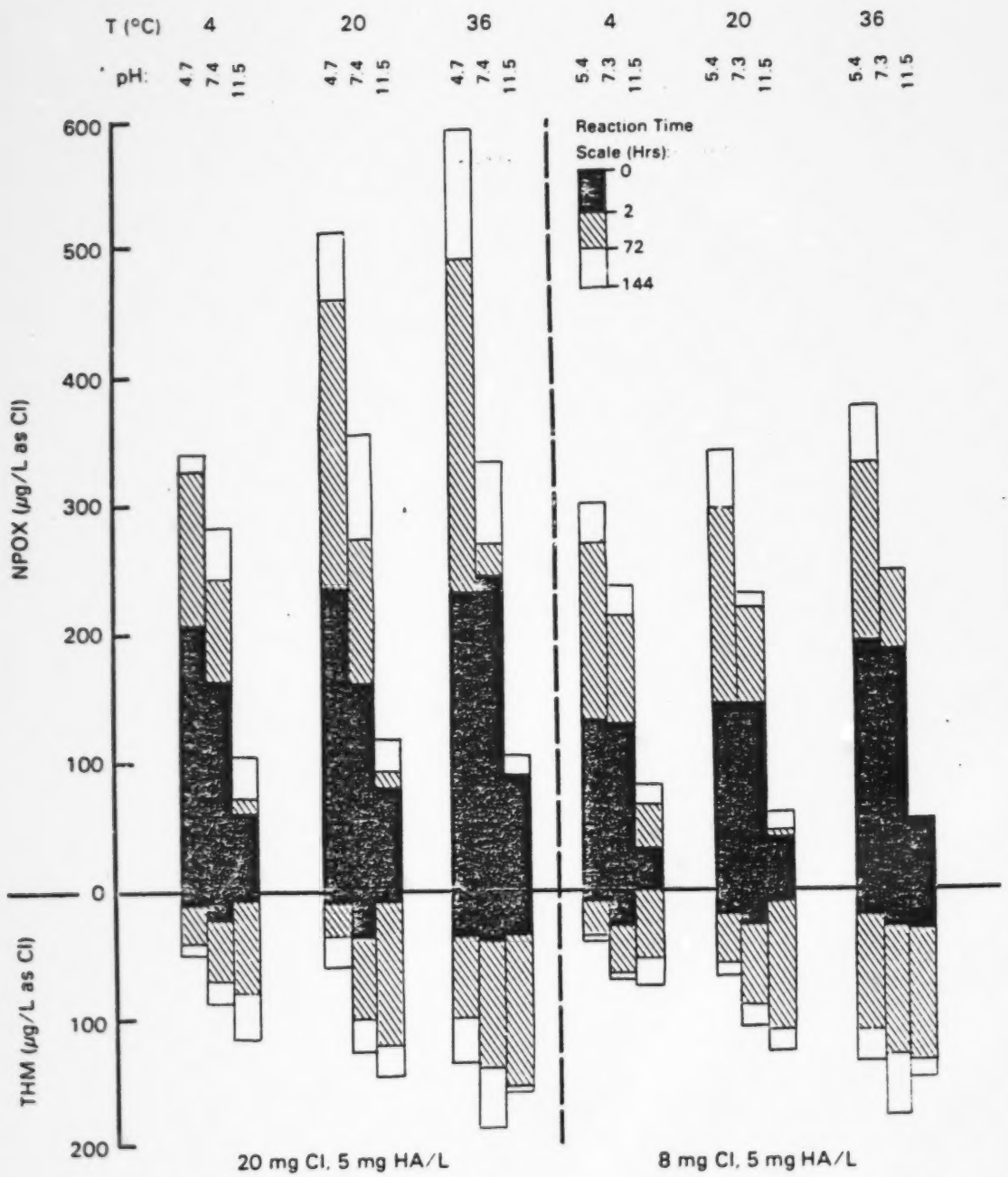

FIG.1 Reaction of Humic Acid at Two Chlorine Doses

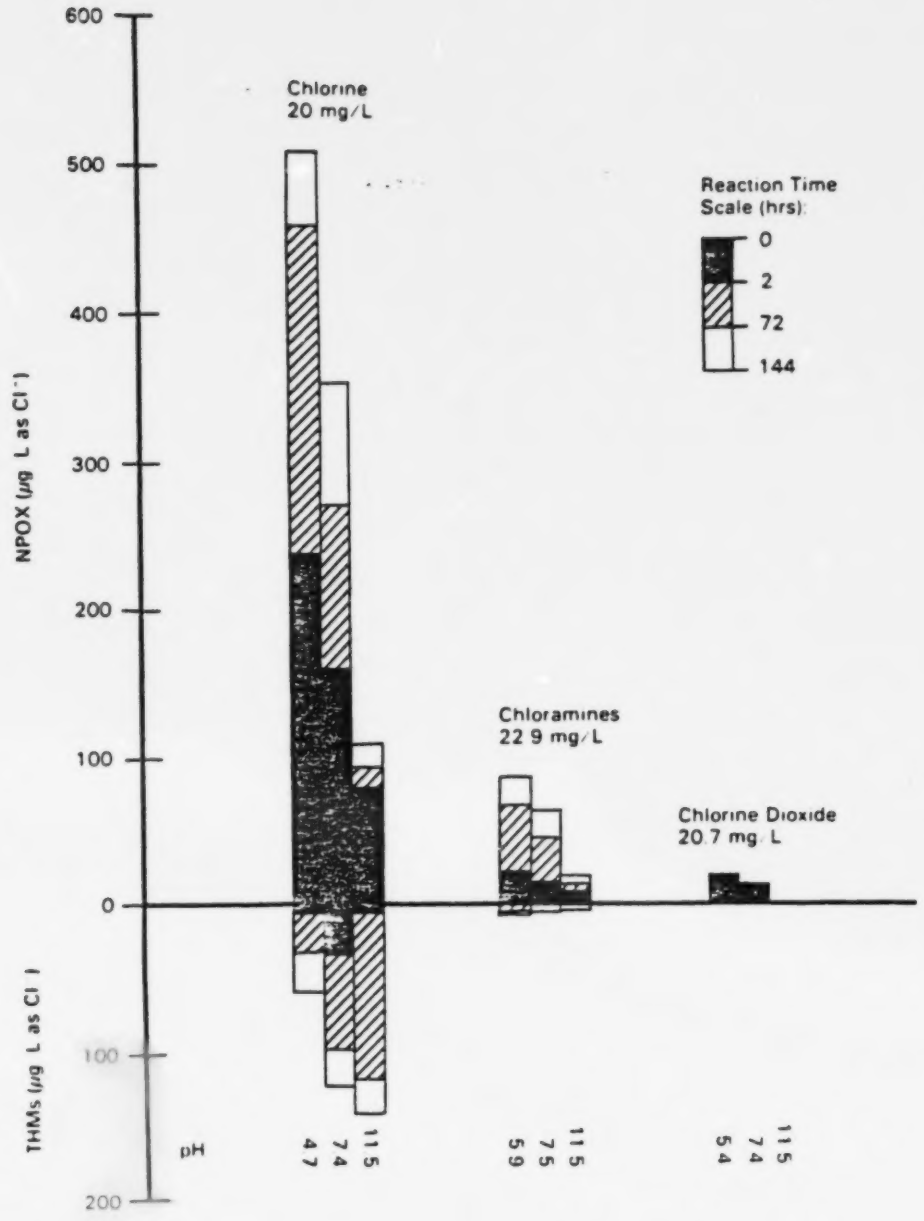

FIG. 2 A Comparison of the Formation of NPOX and THMs ($CHCl_3$) at 20°C in Distilled Water Solutions of 5 mg Humic Acid/L Dosed with Various Disinfectants. Note that NPOX + THMs = TOX (the entire bar).

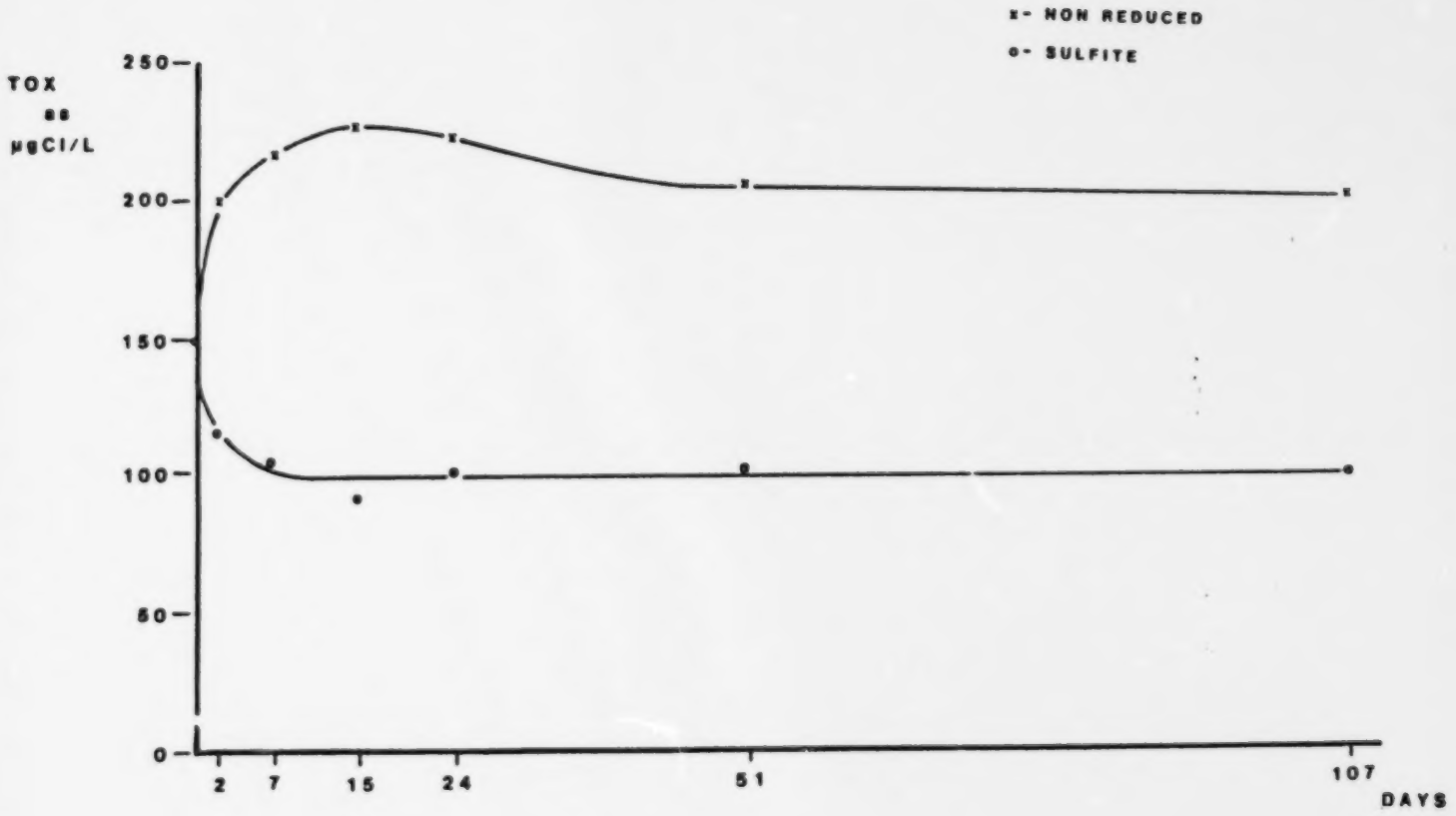

FIG. 3 Time Storage of Cincinnati Tap Water at 20°C